ELEMENTAL AND NMR CHARACTERIZATION OF TARS FROM ENTRAINED-FLOW FLASH PYROLYSIS OF COAL

Muthu S. Sundaram* and Meyer Steinberg
Process Sciences Division
Department of Applied Science
Brookhaven National Laboratory
Upton, NY 11973

and

Konda R. Ramalingam
Department of Medicinal Chemistry
College of Pharmacy
University of Michigan
Ann Arbor, Michigan 48109

ABSTRACT

A New Mexico sub-bituminous coal was flash pyrolyzed in an He atmosphere in an entrained downflow tubular reactor at temperatures from 700°C to 1000°C and at 50 psi. In addition to C_1-C_2 gases, CO and BTX, as high as 9.8% of the dry, ash-free coal was converted to tar at 700°C. The tars were characterized via elemental analysis and ^1H NMR spectroscopy. ^1H NMR data show that the structural characteristics of the tars with respect to hydrogen type distribution depend on the severity of the reaction conditions. The non-aromatic hydrogen content of the tars decreased with increase in the pyrolysis temperature whereas the aromatic hydrogen content of the tars followed an opposite trend.

INTRODUCTION

The devolatilization of coal by rapid or flash heating produces primary tar as a result of thermal decomposition and depolymerization of the starting material. The extent of alteration of the physico-chemical properties of the primary devolatilization products via subsequent decomposition reactions depends on the process conditions in the pyrolyzer. For some types of coal, the primary devolatilization may be complete in a very short residence time, i.e., within the first few feet of a reactor. The primary products, if allowed to pass through additional length of a fully heated reactor, undergo extensive secondary reactions and the quality and quantity of the resulting end products depend on the severity of the reaction conditions.

(1.4)

The effects of various process parameters on the yield and the kinetics of formation of gaseous products and light organic chemicals such as BTX have been studied extensively.[1-3] In most instances, analysis of the above high volatile products were made with the use of on-line GC instrumentation. However, low volatile, high molecular weight and multi-functional tar fraction is complex in nature and requires special handling. It is also noted that the yield of tar fraction is generally low when compared to that of other high volatile products. In consequence, characterization studies on tar from coal pyrolysis experiments are limited.

In an effort to obtain a better picture of the progressive changes that accompany coal devolatilization, we applied several modern analytical techniques to gas, liquid, tar and char products from the pyrolysis of a sub-bituminous coal. In a previous paper, the effects of temperature, residence time and the pyrolysis atmosphere on the yields of gaseous products and BTX were reported.[4] In this paper, we present the results of elemental and ^{1}H NMR characterization of tars from the same set of pyrolysis experiments. The results of capillary-GC/MS and pyrolysis-GC/MS characterization of oil and asphaltene fractions of the tars as well as SEM and FTIR analyses of the chars will be reported elsewhere.

EXPERIMENTAL

Pyrolysis Experiments:

A New Mexico sub-bituminous coal with analysis shown in Table 1 was flash pyrolyzed in a highly instrumented 1-in. I.D. by 8-ft long entrained downflow tubular reactor. The reactor system has been described in detail previously.[5] Multiple analyses of CO_x, C_1-C_2 gases and BTX are made via an on-line GC and the products heavier than BTX are collected in a Freon cooled (~-40°C) condenser. At the end of each experiment, the reactor is washed with vythane and the washings are combined with the contents of the condensers. From the liquid mixture, vythane is distilled off in a rotory evaporator to obtain the tar product.

Analytical Characterization:

A Perkin-Elmer elemental analyzer was used to determine the elemental composition of tars. The C, H and N content of the tars were determined directly and (O + S) was obtained by difference.

Proton-NMR spectra at 60 MHz were obtained with a Varian Model EM-360 Spectrometer. The samples were dissolved in $CDCl_3$ and the spectra were recorded at an ambient temperature of ~25°C with tetramethylsilane (TMS) as internal standard reference.

RESULTS AND DISCUSSION

Figure 1 shows the percent carbon conversion to CH_4, C_2H_4, CO_x and BTX as a function of temperature and residence time. At all residence times, the yield of ethylene maximized at 900°C, whereas that of CO_x continued to increase with temperature. By taking gas and BTX samples from different sample taps located at every 2-ft length of the reactor, the yield data for these products corresponding to at least four different residence times of the coal particles can be obtained from one single run.

The tar is collected at the end of the run and the yield corresponding to the longest coal particle residence time only is available from a particular run. In the set of experiments reported here, the longest coal particle residence time was 1.5 - 1.6 sec. The tar yield decreased with pyrolysis temperature as shown in Figure 2. Roughly half of the tar was made up of hexane soluble oil, the remaining being hexane-insoluble but benzene-soluble asphaltenes.

The effect of pyrolysis temperature on the absolute elemental composition of unfractionated tars is shown in Figure 3. There is a marked difference in the elemental composition of the tars obtained at 700° and 800°C. Particularly noticeable is the difference in oxygen content of these tars. At temperatures higher than 800°C, there is no significant variation in the elemental composition of tars.

Weighted distribution of C, H, N and O in tar can be more useful than the elemental composition alone. This is obtained by taking the elemental analysis data together with the tar yields. From a knowledge of coal feed rate and the weighted elemental distribution in tar, one can determine the actual amount of a particular element that remains in the tar as percent of original feed. The overall expression can be written as follows:

$$\%Conv._{X_{tar}} = \frac{\%X_{tar} \times W_{tar}(gm)}{r_{coal}(gm/min) \times t_r(min) \times [\%X_{coal}(1-a)]}$$

where,

$\%X_{tar}$	=	Percent composition of element X in tar
W_{tar}	=	Amount of tar collected
r_{coal}	=	Coal feed rate
t_r	=	Duration of coal feed
$\%X_{coal}$	=	Percent composition of element X in coal
a	=	Fraction of ash in coal
$\%Conv._{X_{tar}}$	=	Percent of element X in original feed that remains in tar

Figure 4 shows the effect of temperature on the calculated amounts of total C, H, N and (O+S) remaining in tar. Most of the decline in the retention of elements in tar occurs between 700° and

800°C. The quality and quantity of tar is almost unaffected on in-
creasing the pyrolysis temperature from 900° to 1000°C. The ease of
removal of elements from tar follows the order: O>H>C>N.

In Figure 1, it was noticed earlier that the carbon conversion to
gases and BTX increased with temperature. This increase in gases and
BTX yields is found to be attributed to the secondary decomposition
reactions of the tar rather than to additional coal devolatilization.
This is shown in Figure 5, in which total carbon conversion to all
products (hydrocarbon gases + CO_x + BTX + tar) is plotted against tem-
perature. There is no significant change in carbon conversion as the
temperature is increased from 700° to 1000°C. Thus, in the case of
pyrolysis of coal in the presence of an inert gas, such as helium, de-
volatilization is almost complete by 700°C, the lowest temperature
used in the BNL reactor. The tar yield has been reported to maximize
at 600°C in the case of pyrolysis of a Texas lignite in a continuous
bench-scale reactor[6].

^{1}H and ^{13}C NMR spectroscopy has been widely used to characterize
coal-derived liquids[7-10]. The ^{1}H NMR spectra (60 MHz) of the tars
derived from the BNL reactor are shown in Figure 6. The assignment of
a given chemical shift range to a particular type of hydrogen is based
on the suggestions by Stompel and Bartle[11]. The percentage distri-
bution of hydrogen under a given category is obtained by dividing the
area integrated within the chemical shift range corresponding to that
category by total area integrated.

The calculated ^{1}H-NMR hydrogen distribution in tars is listed in
Table 2. The effect of temperature on hydrogen distribution is graph-
ically shown in Figure 7. The aromatic hydrogen distribution in the
tars increases with pyrolysis temperature, whereas there is a decrease
in all other forms of hydrogen. The main difference between different
curves is in their slopes. The only exception is hydrogen in β-posi-
tion to an aromatic ring, the distribution of which is not affected by
temperature.

The actual amount of aromatic hydrogen and non-aromatic hydrogen
(phenolic hydrogen + aliphatic hydrogen) in tar can be calculated from
the ^{1}H NMR hydrogen distribution data, % hydrogen content of the tar
and the tar yield. The actual amounts of aromatic and non-aromatic
hydrogen in tar are plotted against temperature in Figure 8. The ac-
tual amounts of both types of hydrogen decrease with increase in tem-
perature, the trend being similar to the one noted in Figure 4.

CONCLUSION

A series of flash pyrolysis conclusion experiments with a New
Mexico sub-bituminous coal in a downflow entrained tubular reactor
shows that the devolatilization process is complete by 700°C in a he-
lium atmosphere. Further increase in temperature causes the secondary
cracking of tar leading to the formation of lighter products without
enhancing devolatilization itself. The ease of removal of elements

from pyrolysis tar as a function of temperature follows the order: O>H>C>N. On a compositional basis, the distribution of aromatic hydrogen in tars increased with temperature, whereas that of all other forms of hydrogen followed an opposite trend. However, the actual amounts of all forms of hydrogen present in total tar decreased with increase in pyrolysis temperature.

ACKNOWLEDGMENT

REFERENCES

1. Howard, J.B., Peters, W.A., and Serio, M.A., "Coal Devolatilization Information for Reactor Modeling: Assessment of Data and Apparatus Availability with Recommendations for Research", EPRI Report No. AP-1803, Res. Proj. No. 986-5, Palo Alto, CA. (1981).

2. Gavalas, G.R., Coal Pyrolysis. Elsevier, New York, pp 39-69 (1982).

3. Talwalker, A.T., A Topical Report in Coal Pyrolysis. Report No. DOE/MC/19136-1408, 1983.

4. Sundaram, M.S., Steinberg, M., and Fallon, P.T., ACS Fuel Div. Prepr., 30 (1985).

5. Sundaram, M.S., Steinberg, M., and Fallon, P.T., "Flash Hydropyrolysis of Coals for Conversion to Liquid and Gaseous Fuels: Summary Report", DOE/METC/82-48 (1982). BNL Report No. 51537.

6. Calkins, W.H., ACS Fuel Div. Prepr., 28(5), 85 (1983).

7. Retwfsky, H.L. and Link, T.L., High Resolution ^{1}H-,^{2}H-, and ^{13}C-NMR in Coal Research, 22, Analytical Methods for Coal and Coal Products, Vol. II.

8. Petrakis, L., Young, D.C., Ruberto, R.G., and Gates, B.C., Ind. Eng. Chem. Proc. Des. Dev., 22, 298 (1983).

9. Young, D.C. and Galya, L.G. Presented at the 189th ACS National Meeting, Div. Pet. Chem., Paper No. 51, Miami, FL, April 28 - May 3, 1985.

10. Allen, D.T., Presented at the 189th ACS National Meeting, Div. Pet. Chem., Paper No. 52, Miami, FL, April 28-May 3, 1985.

11. Stompel, Z.J., and Bartle, D., Fuel, 62, 900 (1983).

TABLE 1. ANALYTICAL DATA FOR NEW MEXICO SUB-BITUMINOUS COAL

Ultimate Analysis	(wt % dry)	Ultimate Analysis	(dry)
Carbon	: 55.9	Volatile Matter	: 34.9
Hydrogen	: 4.3	Fixed Carbon	: 42.4
Nitrogen	: 1.1	Ash	: 22.8
Sulfur	: 1.0		
Oxygen (by diff.)	: 14.9		

TABLE 2. FLASH PYROLYSIS OF NEW MEXICO SUB-BITUMINOUS COAL
50 psi HELIUM, 1.5 sec RESIDENCE TIME

HYDROGEN DISTRIBUTION IN TAR FRACTIONS (^{1}H NMR)

| Hydrogen Type	^{1}H Chemical Shift Range (ppm from TMS)	Temperature, $^\circ$C			
		700	800	900	1000
Aromatic	6.5-9.0	27.4	43.9	57.5	64.7
Phenolic	5.5-6.5	5.7	3.9	2.3	1.5
Olefinic	4.5-5.5	9.4	6.1	2.3	1.5
Benzylic	3.3-4.5	11.3	8.8	4.6	4.4
CH_3,CH_2, and CH-α to an aromatic ring	2.0-3.3	24.5	19.9	17.1	11.8
CH_2 and CH β to an aromatic ring (naphthenic)	1.6-2.0	4.7	2.7	2.6	2.9
β-Ch_3,CH_2 and CH-γ to an aromatic ring	1.0-1.6	12.3	12.0	11.9	11.8
CH_3 γ or further from an aromatic ring	0.5-1.0	4.7	2.7	1.8	1.5
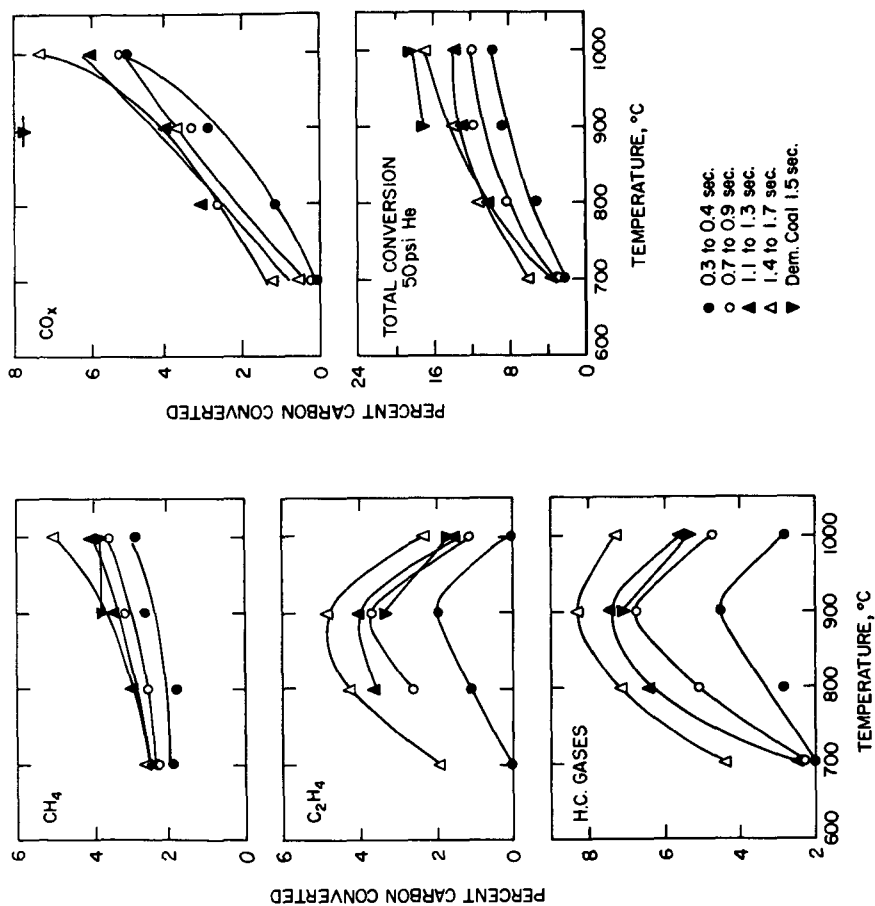
Figure 1. Effect of Temperature on Carbon Conversion to Gases and BTX.

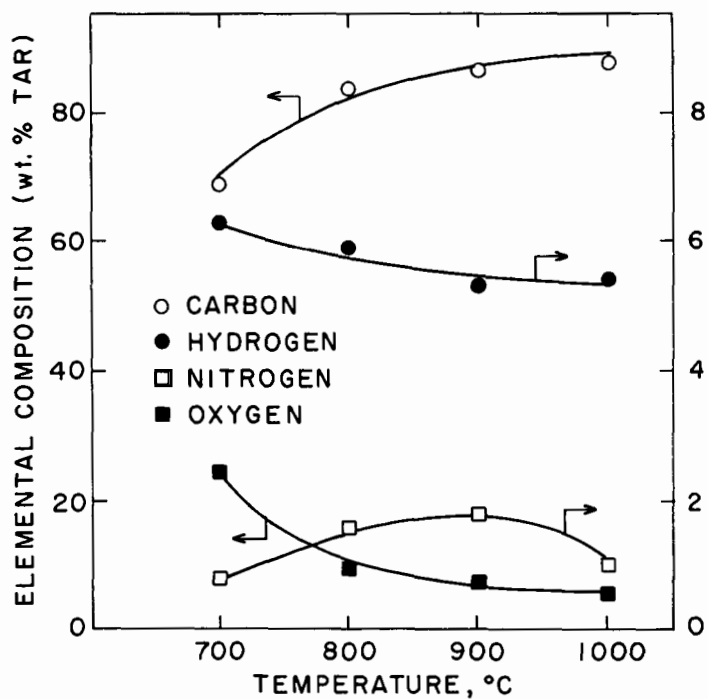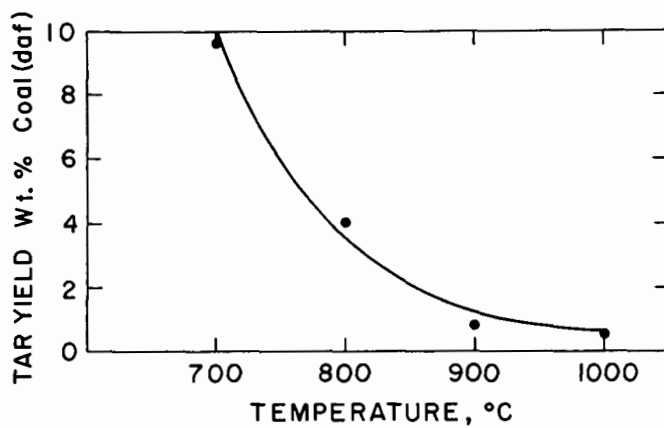Figure 2.   Effect of Temperature on Tar Yield.

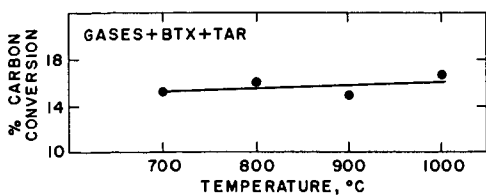Figure 3.   Effect of Temperature on Elemental Composition of Tar.

Figure 5. Effect of Temperature on Total Carbon Conversion to Gases, BTX, and Tar.
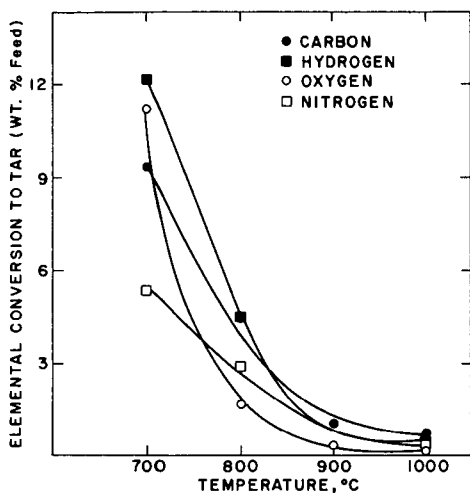

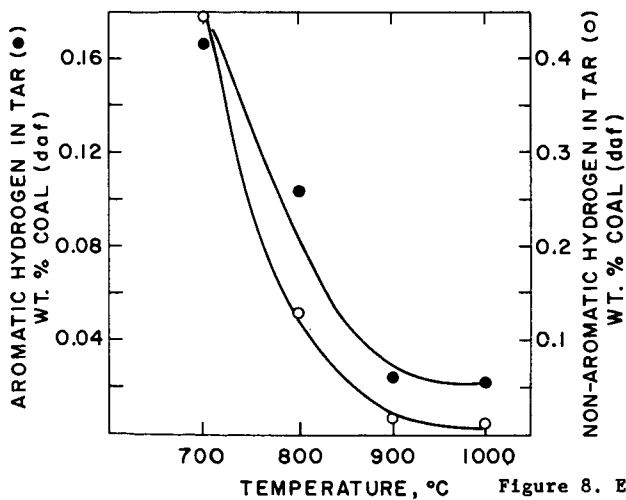Figure 4. Effect of Temperature on Elemental Conversion to Tar.

Figure 8. Effect of Temperature on Total Aromatic and Total Non-Aromatic Hydrogen in Tar.
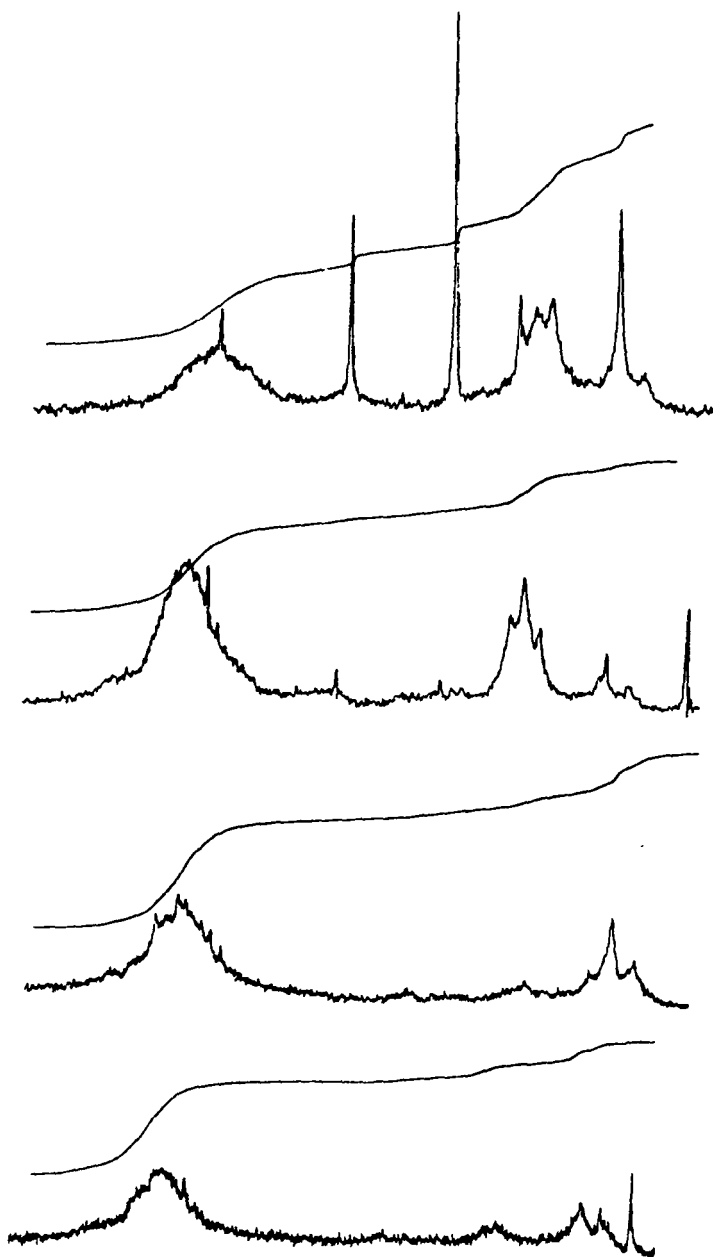
Figure 6.   60 MHz ¹H NMR Spectra of Pyrolysis Tars.

241

¹H NMR HYDROGEN DISTRIBUTION IN TAR

(NEW MEXICO SUB-BITUMINOUS COAL)

50 psi He @ 1.5 sec

- ● AROMATIC
- ◐ PHENOLIC
- × OLEFINIC
- □ BENZYLIC
- ○ α-CH,CH$_2$,CH$_3$
- ■ β-CH,CH$_2$
- △ β-CH$_3$,γ-CH,CH$_2$
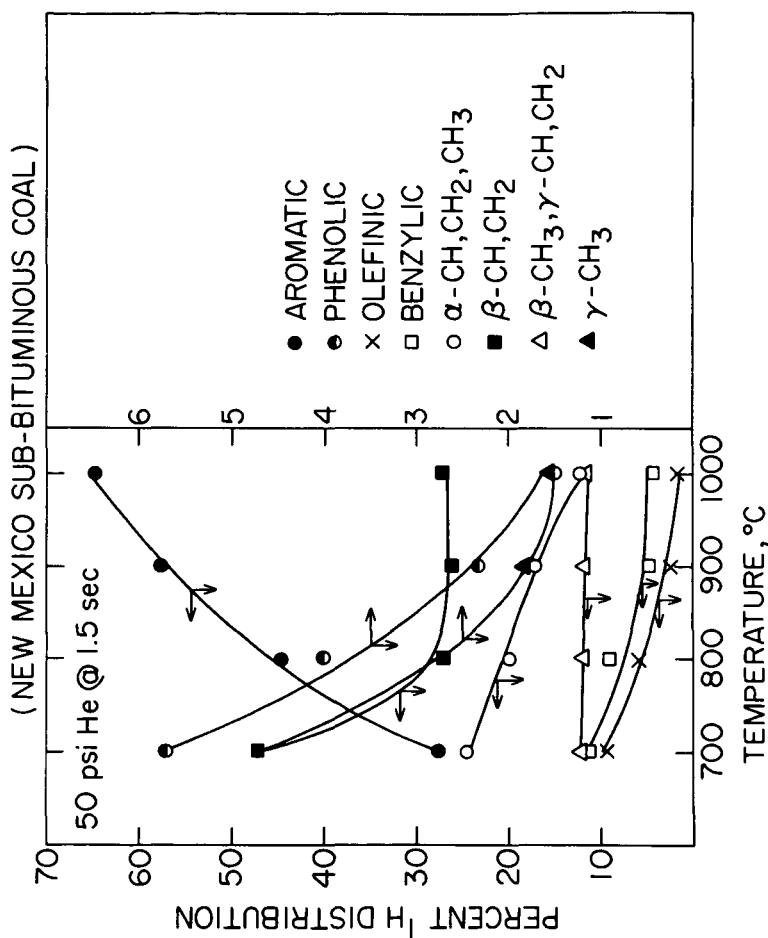- ▲ γ-CH$_3$

PERCENT ¹H DISTRIBUTION

TEMPERATURE, °C

Figure 7. Effect of Temperature on Hydrogen Distribution in Tar.